

LA-UR- 04-4610

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*Title:* MULTIPHASE FLUID-ROCK REACTIONS  
AMONG SUPERCRITICAL CARBON DIOXIDE, BRINE,  
AQUIFER, AND CAPROCK: RELEVANCE TO GEOLOGIC  
SEQUESTRATION OF CARBON

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*Submitted to:* 11th International Symposium & Exhibit on Supercritical Fluid  
Chromatography, Extraction, & Processing



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Form 836 (8/00)



**Multiphase Fluid-Rock Reactions  
among Supercritical Carbon Dioxide, Brine, Aquifer, and Caprock:  
Relevance to Geologic Sequestration of Carbon**

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The reactive behavior of a multiphase fluid (supercritical CO<sub>2</sub> and brine) under physical-chemical conditions relevant to geologic storage and sequestration in a carbon repository is largely unknown. Experiments were conducted in a flexible cell hydrothermal apparatus to evaluate multiphase fluid-rock (aquifer plus caprock) reactions that may impact repository integrity.

A carbon repository will exhibit a wide range of temperature and pressure, approximately 50-200°C and 20-1000 bars. The temperature of 200°C was selected for these experiments to maximize kinetic rates of silicate reactions. A pressure of 200 bars was chosen for consistency with sequestration scenarios. In one experiment, a 5.5 molal NaCl brine-rock system was reacted for 32 days to approach steady state, then injected with supercritical CO<sub>2</sub> (scCO<sub>2</sub>) and allowed to react an additional 45 days. In a separate experiment, the brine-rock system reacted for 77 days without scCO<sub>2</sub>. In a third experiment, the rock reacted with 5.5M Mg-NaCl brine for 59 days. CO<sub>2</sub> was then injected and the system allowed to react for an additional 80 days. Thus, the selected brines present a range of reaction potential among rock, brine, and scCO<sub>2</sub>. On one hand, carbonate mineral may readily precipitate from Mg-rich brine containing aqueous carbonate ion buffered by coexisting scCO<sub>2</sub> (Kaszuba et al., 2003). On the other, the Na-rich brine, initially devoid of divalent cations, can only derive the cations needed for carbonate precipitation by reaction with silicate minerals. In all experiments, reservoir rock (K-feldspar, Na-Ca feldspar, quartz and Fe-Mg mica) and a cap rock (clay-rich shale) are part of the reactive system.

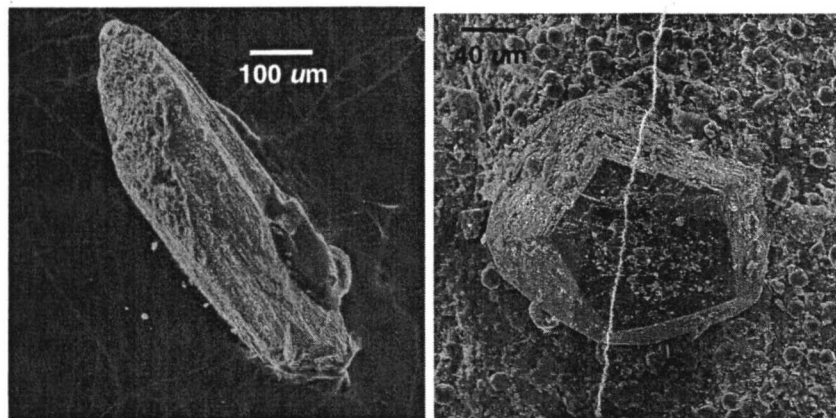


Figure 1. Secondary electron SEM micrographs of magnesite (on left) and siderite (on right) from the NaCl brine-scCO<sub>2</sub>-rock experiment. Magnesite crystals are large, up to a few mm in length, and occur as individual grains and splays. Pitted crystal faces indicate disequilibrium and are interpreted as dissolution of early-formed magnesite. Siderite occurs as individual crystals, about 200-250 µm in diameter, growing on shale. Euhedral texture, indicative of equilibrium, is interpreted as precipitation of siderite after early-formed magnesite. Small, rounded grains surrounding the siderite are euhedral analcime. After Kaszuba *et al.*, 2004, in review.

Magnesite (MgCO<sub>3</sub>) precipitated in the Mg-NaCl brine-scCO<sub>2</sub>-rock experiment whereas magnesite and siderite (FeCO<sub>3</sub>) precipitated in the NaCl brine-scCO<sub>2</sub>-rock system (Figure 1). Pitted magnesite and euhedral siderite in the latter experiment may suggest a paragenetic sequence for stabilization of carbonate phases. Nucleation and growth of siderite on caprock (shale) suggests caprock is a reactive component. Euhedral analcime crystallized in all experiments due to the high activity of Na in the brine.

Changes in brine following addition of CO<sub>2</sub> include pH decrease (1 unit in NaCl brine, 2 units in Mg-NaCl brine, Figure 2) and Na depletion. A pH increase follows pressure and temperature quenching and loss of saturated CO<sub>2</sub> from acidic brine. Silica concentrations and dissolution rates are enhanced and silica precipitation inhibited in the acidic brine. Without added CO<sub>2</sub>, SiO<sub>2</sub> in NaCl and Mg-NaCl brine stabilized near calculated quartz solubility. Injection of CO<sub>2</sub> doubled SiO<sub>2</sub> content to chalcedony solubility by silicate dissolution and inhibition of quartz precipitation.

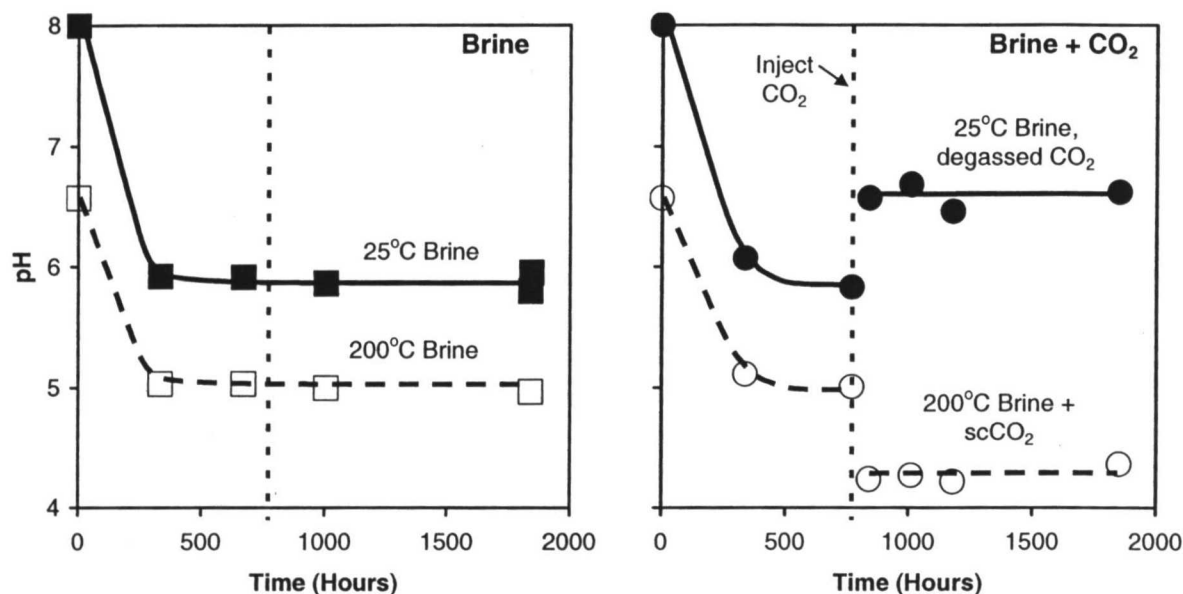


Figure 2. pH behavior during the experimental reaction for brine-rock (at left) and scCO<sub>2</sub>-brine-rock (at right). For both, pH is measured at 25°C, 1 bar in samples from which CO<sub>2</sub> has degassed (solid lines and symbols). Calculation of pH using Geochemist's Workbench and the b-dot ion association model (Bethke, 1998) for brine samples at 200°C indicates an in-situ pH (dashed lines and open symbols). In both experiments, in-situ pH decreases from 6.6 to approximately 5 by the time the first sample is collected. Following injection of CO<sub>2</sub> into the scCO<sub>2</sub>-brine-rock experiment, in-situ pH further decreases to approximately 4.2 (open circles). At 25°C, pH measured in degassed brine from this experiment is approximately 6.6 (solid circles). Uncertainties are equal to the size of the symbols. After Kaszuba *et al.*, 2004, in review.

Geochemical reactions in a carbon repository extend beyond pH decrease and carbonate mineral precipitation. Rock-dominated reaction systems yield to fluid-dominated systems with acidic brine and multiphase fluid reactions. Silica super-saturation and increased alkalinity associated with multiphase fluid equilibria could be monitored as geochemical indicators of repository performance. Return of silica super-saturated brine to a rock-dominated reaction system buffered to neutral pH may enhance silica precipitation. The potential effects (beneficial or deleterious) that silica super-saturation and precipitation may hold for repository performance are not known.

## References:

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